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(54) Title: CONSTRUCTIVE NANOLITHOGRAPHY

(57) Abstract: A patterned organic monolayer or multilayer film self-assembled on a solid substrate, the pattern consisting in a site-defined surface chemical modification non-destructively inscribed in the organic monolayer or multilayer by means of an electrically biased conducting scanning probe device, stamping device and/or liquid metal or metal alloy or any other device that can touch the organic monolayer or multilayer surface and inscribe therein a chemical modification pattern upon application of an electrical bias.

[illegible]

[illegible]

2B

[illegible]

[illegible]

[illegible]

2θ

p [illegible] m [illegible] A [illegible] m [illegible]

silver grains generated in the initial Ag^+ reduction step was accomplished with a commercial silver enhancer solution (Sigma, Silver Enhancer Kit) which was further diluted with pure water when lower metal deposition rates were desired. Drops of the enhancer solution were placed on the template surface for the specified periods of time, then removed and the surface rinsed with drops of pure water. The removal of the drops was done by suction with a sharp pipette without any visible traces of liquid being left on the surface, due to the relatively high hydrophobicity of the TFSM surface. Thus, the water contact angles characteristic of TFSMs obtained from mixed precursor monolayers with a molar ratio NTS/OTS = 1/2 vary from ca. 70^o(adv.) and 64^o (rec.) on the silver-free surface, to ca. 67^o (adv.; rec.) on the surface fully loaded with Ag^+ ions.

The post-patterning chemical modification and self-assembly operations involving liquid reagents were done with drops of the desired solution being placed on the patterned monolayer surface (without removing the sample from the microscope stage), followed by drops of a suitable rinsing solvent. For the self-assembly of the NTS overlayer (**Figs. 1, 4-6**), a drop of water was first placed on the surface for ca. 2 min, then a drop of a 5 mM solution of NTS in BCH (for ca. 2 min), and final rinse with two drops of pure BCH followed by two drops of decalin, the NTS adsorption and the solvent rinses being repeated twice. Since none of the liquids employed wet the OTS monolayer, removal of the drops was simply done by suction, without any visible traces of material being left on the surface.

For the conversion of NTS to TFSM, the sample was irradiated (Hg lamp, λ= 254 nm) for 10 min in a H_2S/Ar (1:1) atmosphere, then rinsed with pure argon and finally twice sonicated (for ca. 15s each) in pure toluene. Both the NTS and TFSM overlayers successfully withstand Scotch tape peeling, which was_routinely applied in order to improve the AFM images by removal of adventitious contamination from the surface. For the formation of CdS, the TFSM surface was loaded with Cd^{2+} ions from a 1 mM solution of cadmium acetate in water (2 min adsorption, followed by rinse with two drops of pure water) and then exposed for 10 min to the same H_2S/Ar atmosphere (without irradiation) followed by the argon rinse. The deposition of

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

p

[illegible]

[illegible]

[illegible]

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[illegible]

23. A method for the production of hybrid metal-organic nanostructures according to claim 18, by template-controlled self-assembly strategy, comprising:

(i) assembling a monolayer of a silane compound terminated by a functional group such as –SH and/or –S-S- on a solid substrate;

(ii) binding a metal ion such as Ag^+ to the functional group of (i); and

(iii) non-destructively patterning the top surface of said metal ion-terminated layer of (ii) by means of an electrically biased conducting scanning probe device, stamping device and/or liquid metal or metal alloy or any other device that can touch said organic monolayer surface and inscribe therein a chemical modification pattern upon application of an electrical bias, thus forming the pattern by site-defined reduction of the metal ions to elemental metal particles.

24. The method according to claim 23, which comprises further developing the elemental metal particles to form self-assembled metal islands or metal films.

25. A method for the production of hybrid inorganic-organic or organic-organic nanostructures according to claim 18, by template-controlled self-assembly strategy, comprising:

(i) assembling a monolayer of a silane compound terminated by a methyl group, on a solid substrate;

(ii) non-destructively patterning the top surface of said methyl-terminated layer of (i) by means of an electrically biased conducting scanning probe device, stamping device and/or liquid metal or metal alloy or any other device that can touch said organic monolayer surface and inscribe therein a chemical modification pattern upon application of an electrical bias, thus forming the pattern by electrochemical site-defined oxidation of the terminal methyl group, for example to an oxygen-containing group such as COOH, and optionally further chemically modifying this oxidized methyl site to another functional group; and

(iii) further generating or binding a metal, metal compound, organic metal or conducting polymer at the modified surface sites of said organic layer of (ii), thus obtaining said nanostructures with a combination of a metal, metal compound,

[illegible]

[illegible]

FIG. 1

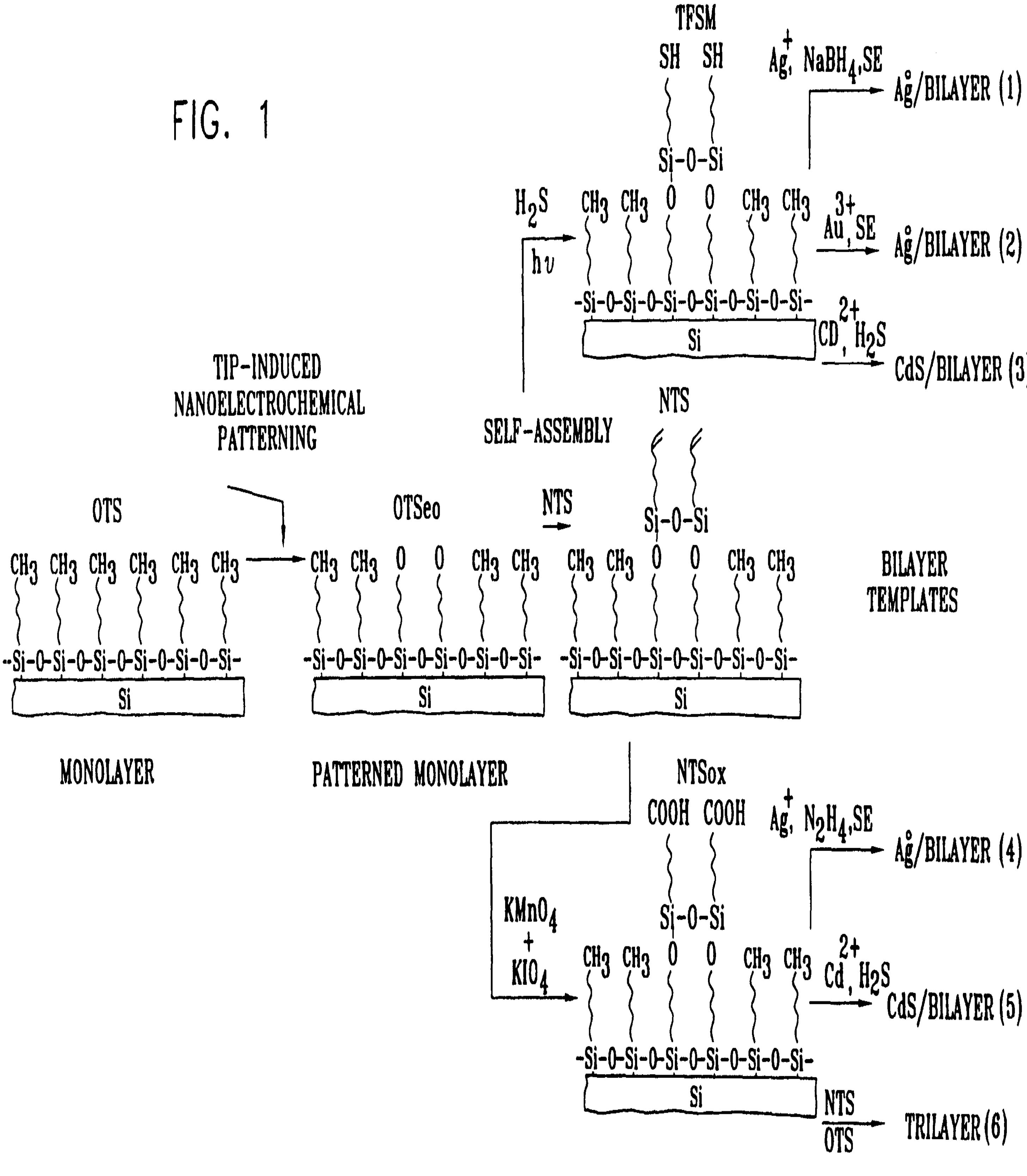
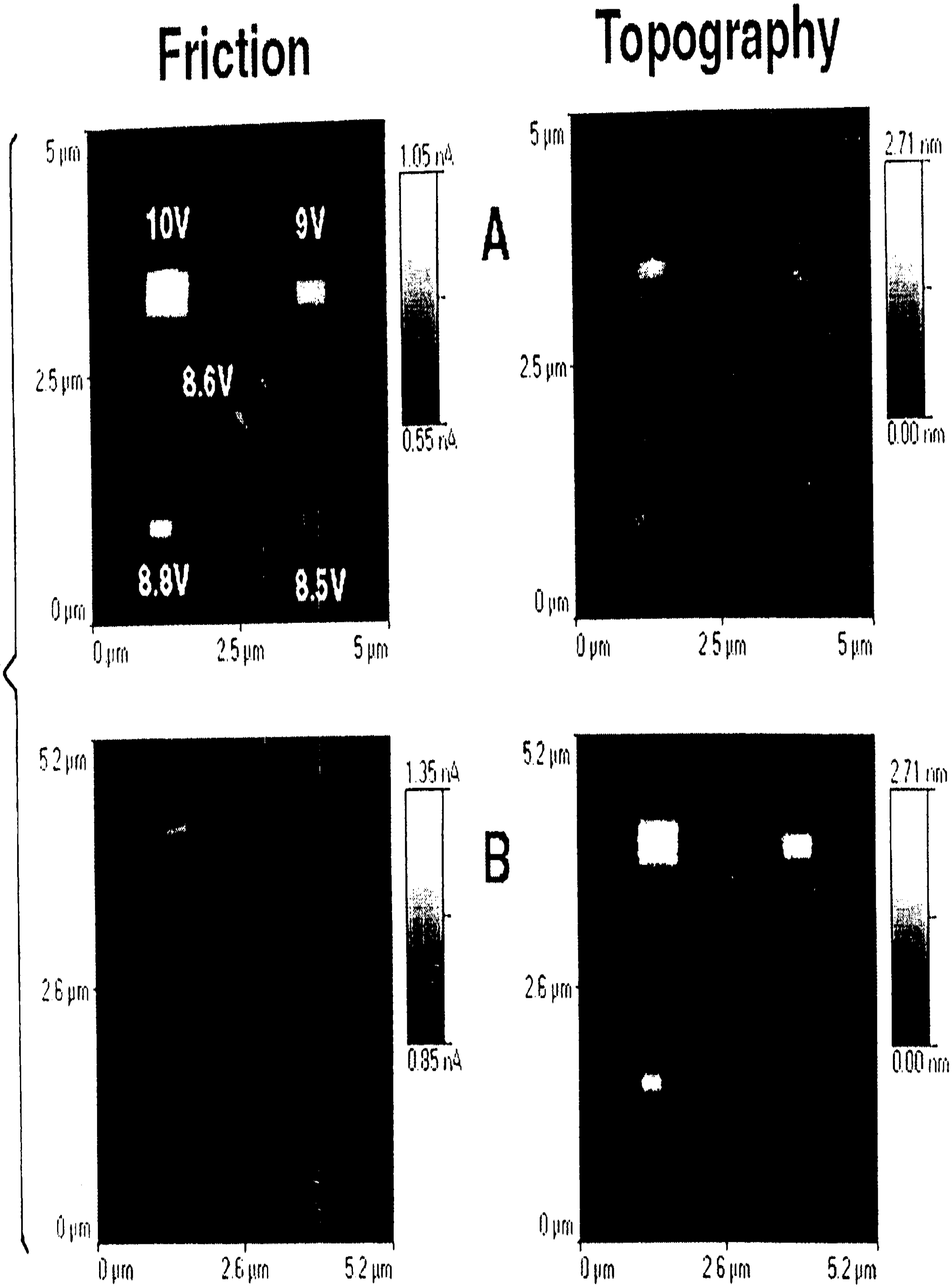
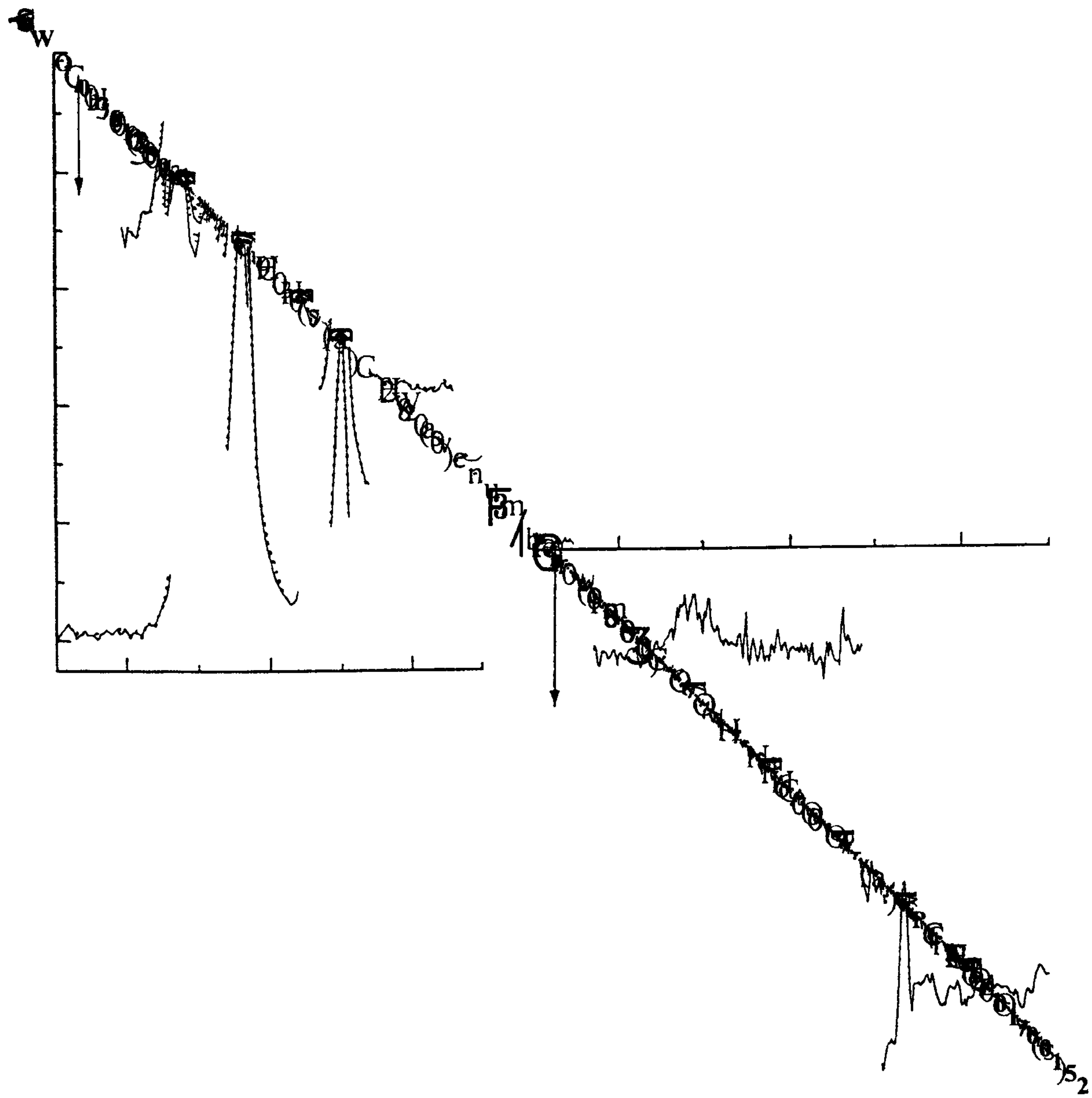

TIP-INDUCED NANOELECTROCHEMICAL PATTERNING
SELF-ASSEMBLY
OTS
OTSeo
NTS
TFSM
NTSox
MONOLAYER
PATTERNED MONOLAYER
BILAYER TEMPLATES
Ag/BILAYER (1)
Ag/BILAYER (2)
CdS/BILAYER (3)
Ag/BILAYER (4)
CdS/BILAYER (5)
TRILAYER (6)

FIG. 2


Friction
Topography
A
B
10V
9V
8.6V
8.8V
8.5V
5 µm
2.5 µm
0 µm
1.05 nA
0.55 nA
2.71 nm
0.00 nm
5.2 µm
2.6 µm
1.35 nA
0.85 nA



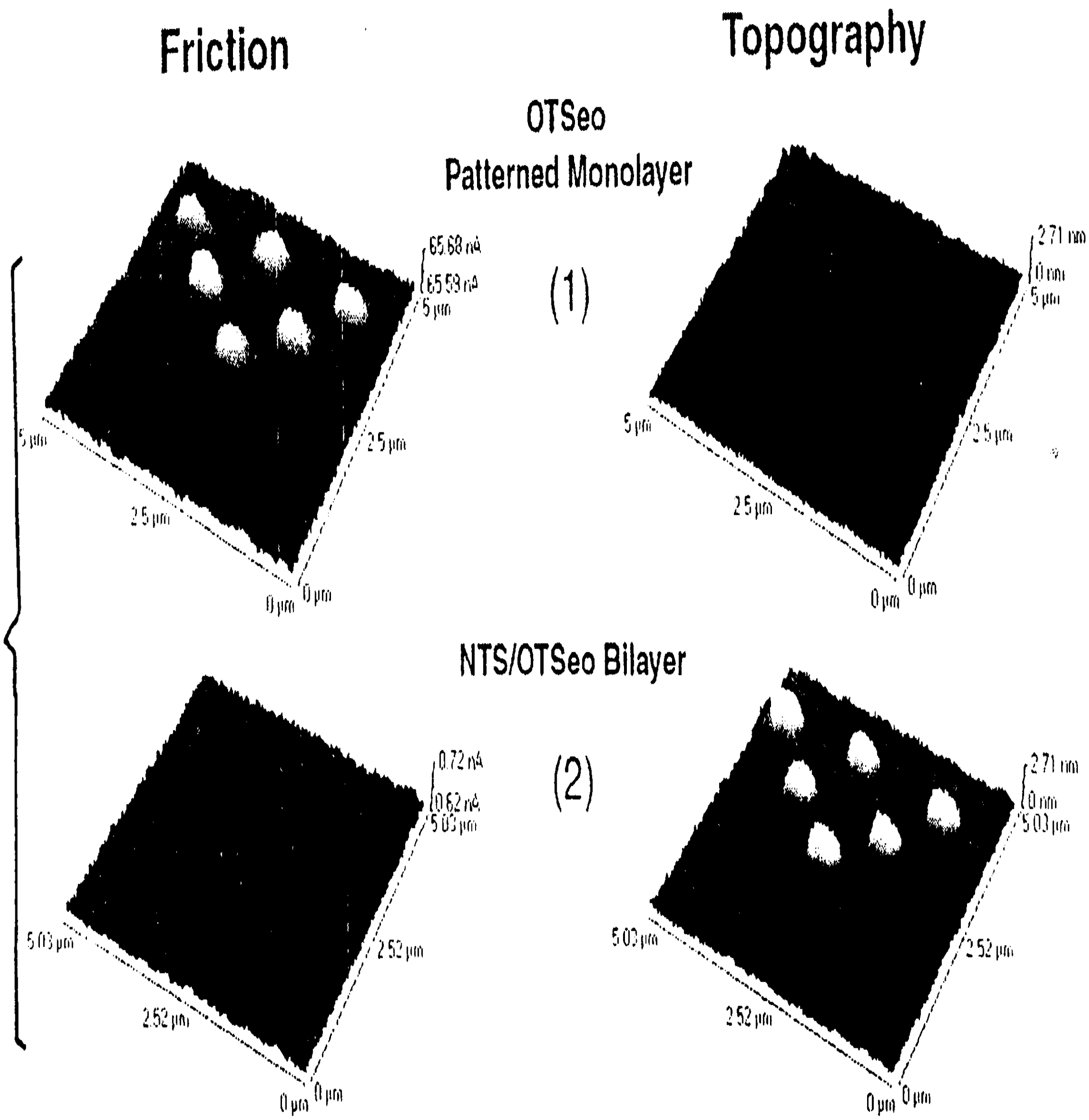
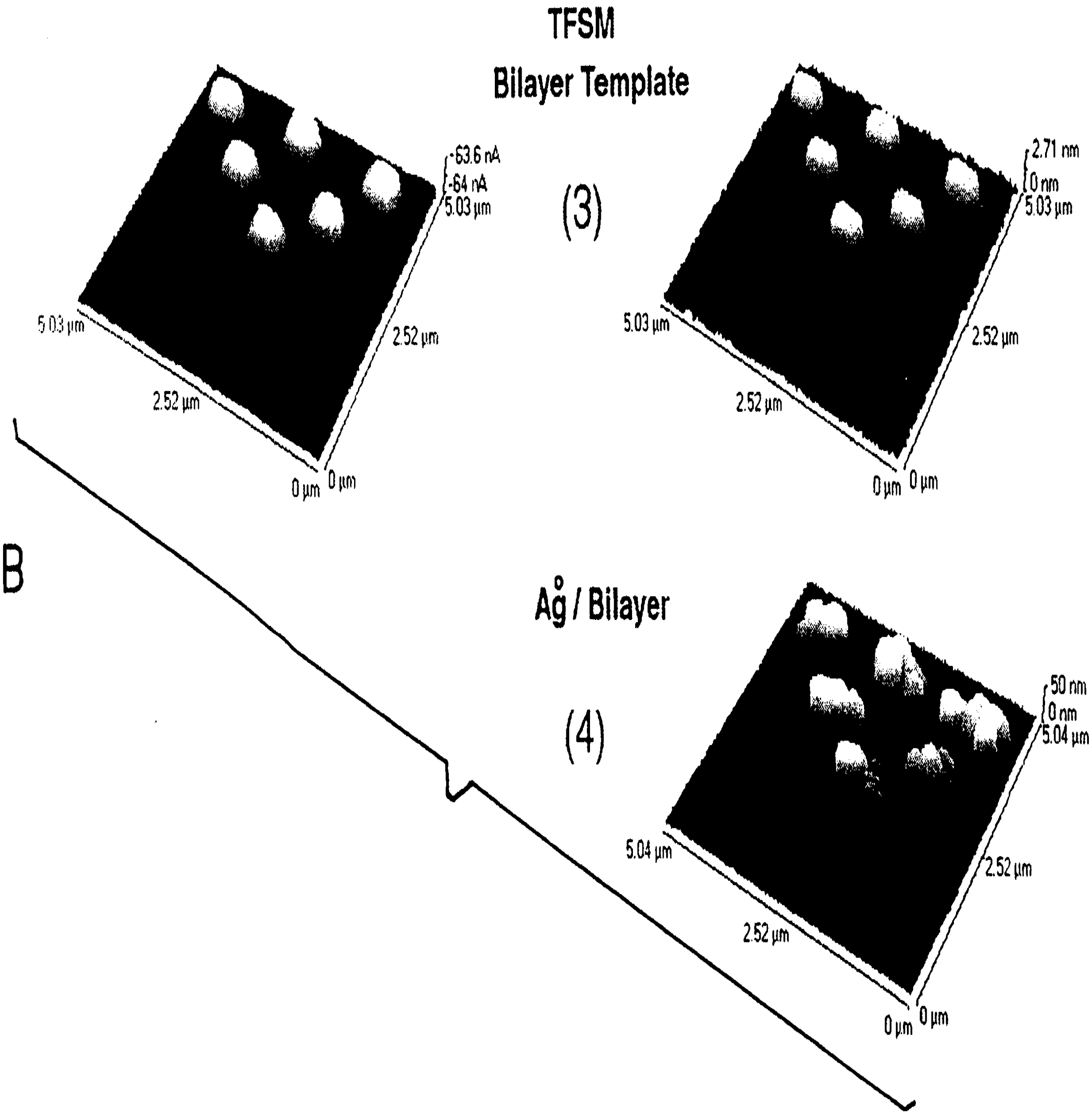

Friction
Topography
OTSeo
Patterned Monolayer
(1)
65.68 nA
65.59 nA
5 μm
2.5 μm
0 μm
2.71 nm
0 nm
NTS/OTSeo Bilayer
(2)
0.72 nA
0.62 nA
5.03 μm
2.52 μm

FIG. 4A

FIG. 4B


TFSM
Bilayer Template
(3)
-63.6 nA
-64 nA
5.03 µm
5.03 µm
2.52 µm
2.52 µm
0 µm
0 µm
2.71 nm
0 nm
5.03 µm
5.03 µm
2.52 µm
2.52 µm
0 µm
0 µm
Ag / Bilayer
(4)
50 nm
0 nm
5.04 µm
5.04 µm
2.52 µm
2.52 µm
0 µm
0 µm

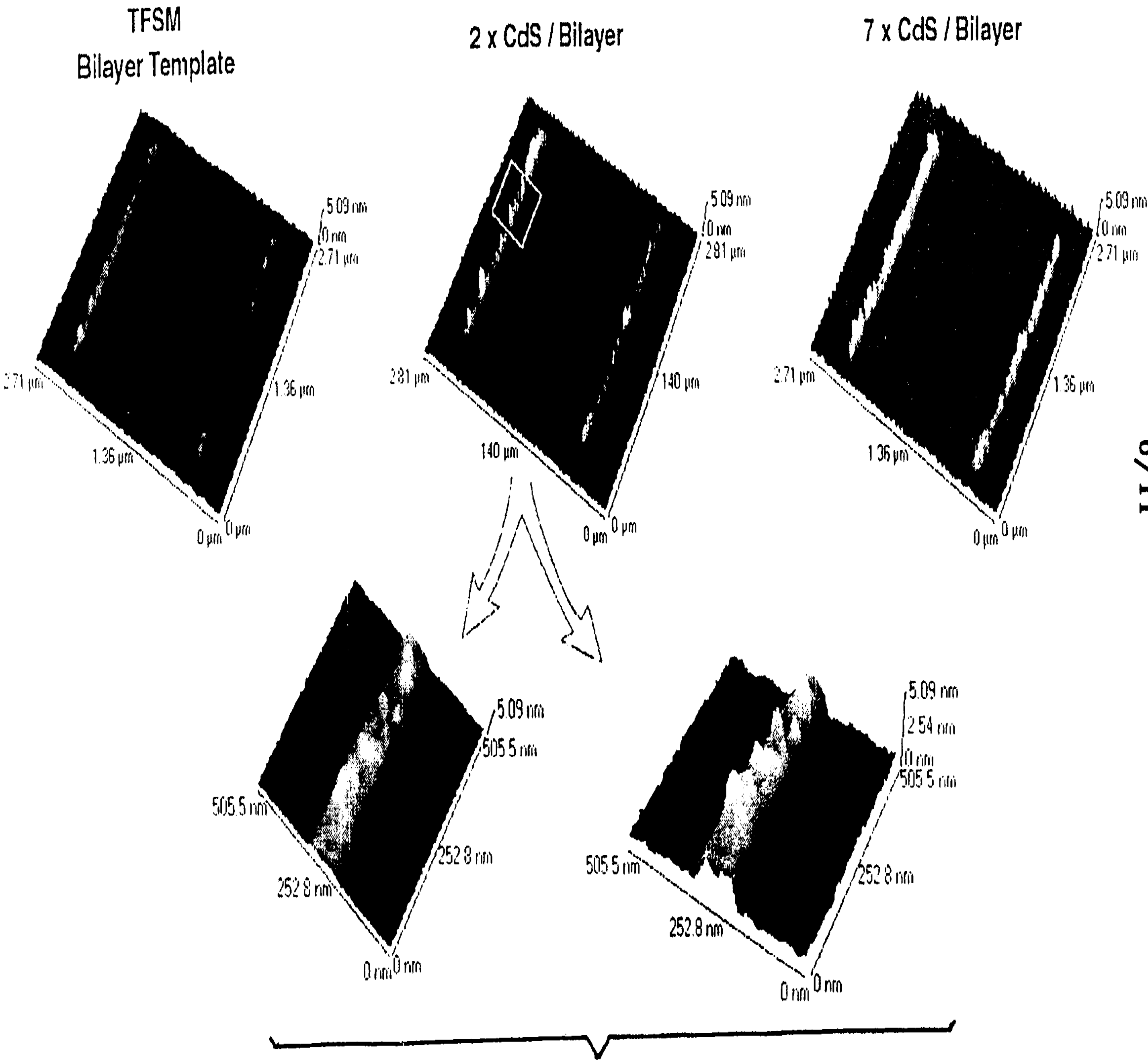

TFSM
Bilayer Template
2 x CdS / Bilayer
7 x CdS / Bilayer
5.09 nm
0 nm
2.71 µm
1.36 µm
0 µm
2.81 µm
1.40 µm
505.5 nm
252.8 nm
2.54 nm
0 nm

FIG. 5

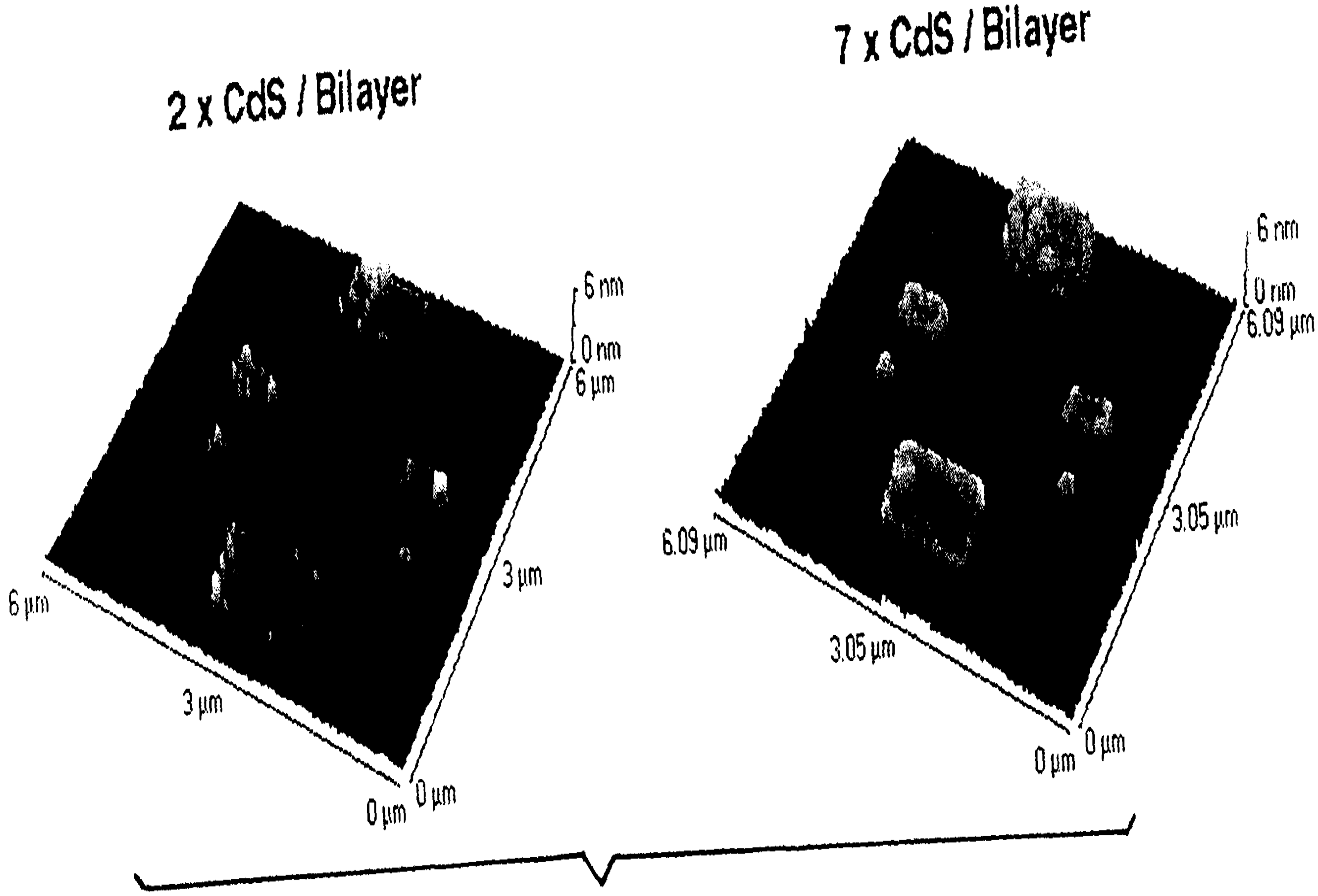
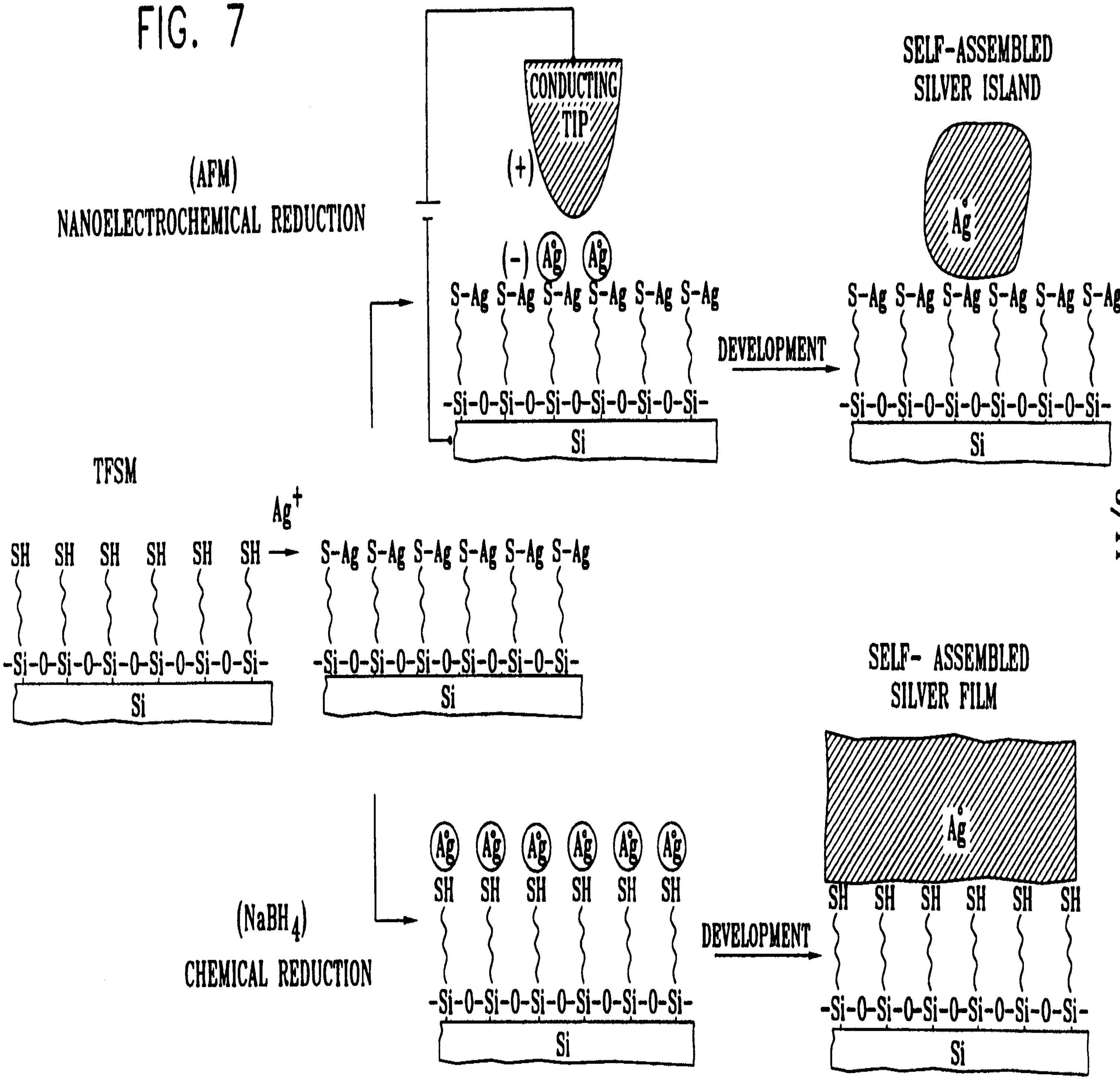

2 x CdS / Bilayer
6 nm
0 nm
6 µm
3 µm
0 µm
0 µm
3 µm
6 µm
7 x CdS / Bilayer
6 nm
0 nm
6.09 µm
3.05 µm
0 µm
0 µm
3.05 µm
6.09 µm

FIG. 6

FIG. 7


(AFM)
NANOELECTROCHEMICAL REDUCTION
CONDUCTING TIP
(+)
(-)
Ag°
S-Ag S-Ag S-Ag S-Ag S-Ag S-Ag
-Si-O-Si-O-Si-O-Si-O-Si-O-Si-
Si
DEVELOPMENT
SELF-ASSEMBLED
SILVER ISLAND
TFSM
SH SH SH SH SH SH
Ag+
SELF- ASSEMBLED
SILVER FILM
(NaBH4)
CHEMICAL REDUCTION

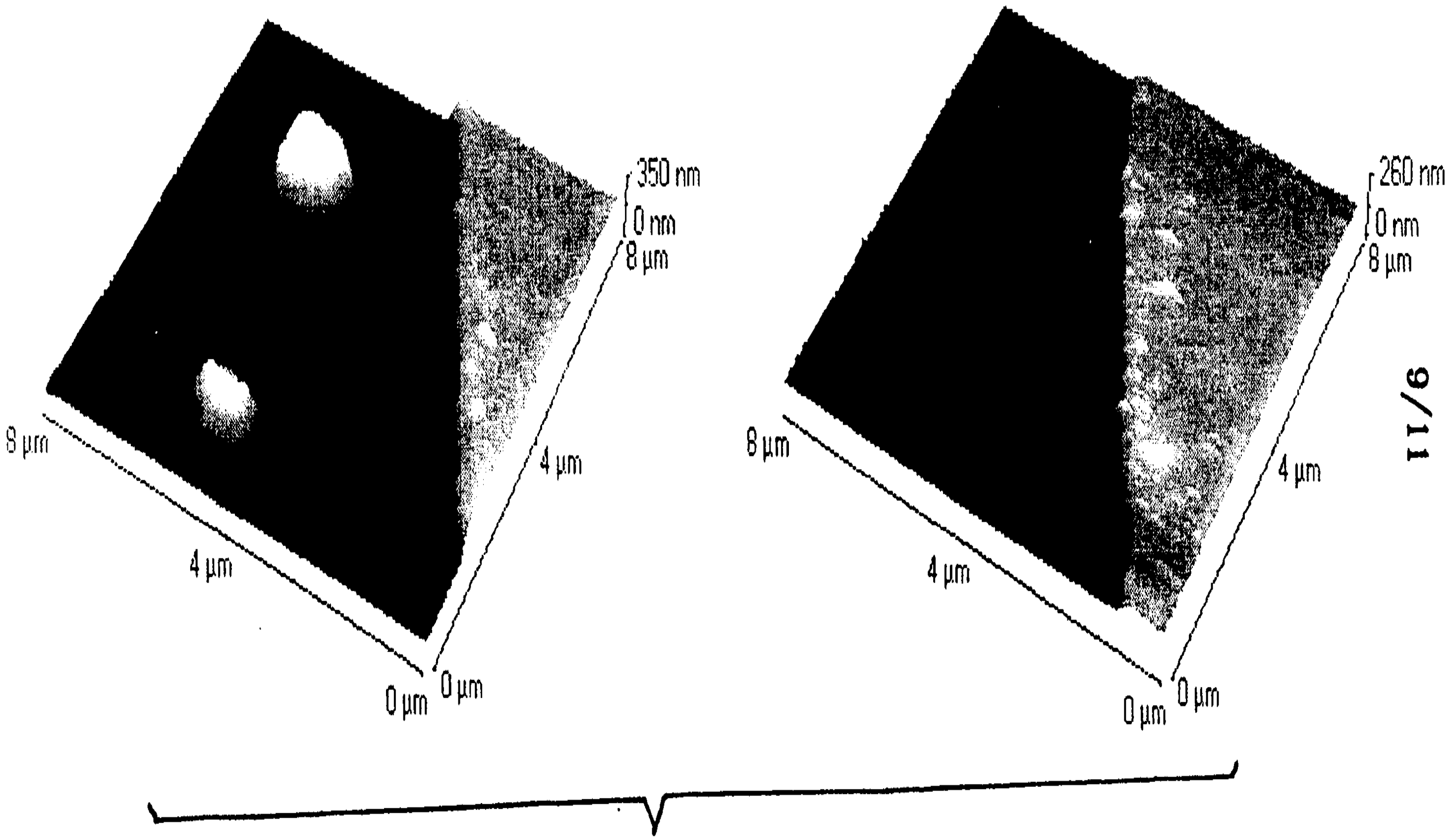

350 nm
0 nm
8 µm
8 µm
4 µm
4 µm
0 µm
0 µm
260 nm
0 nm
8 µm
8 µm
4 µm
4 µm
0 µm
0 µm

FIG. 8

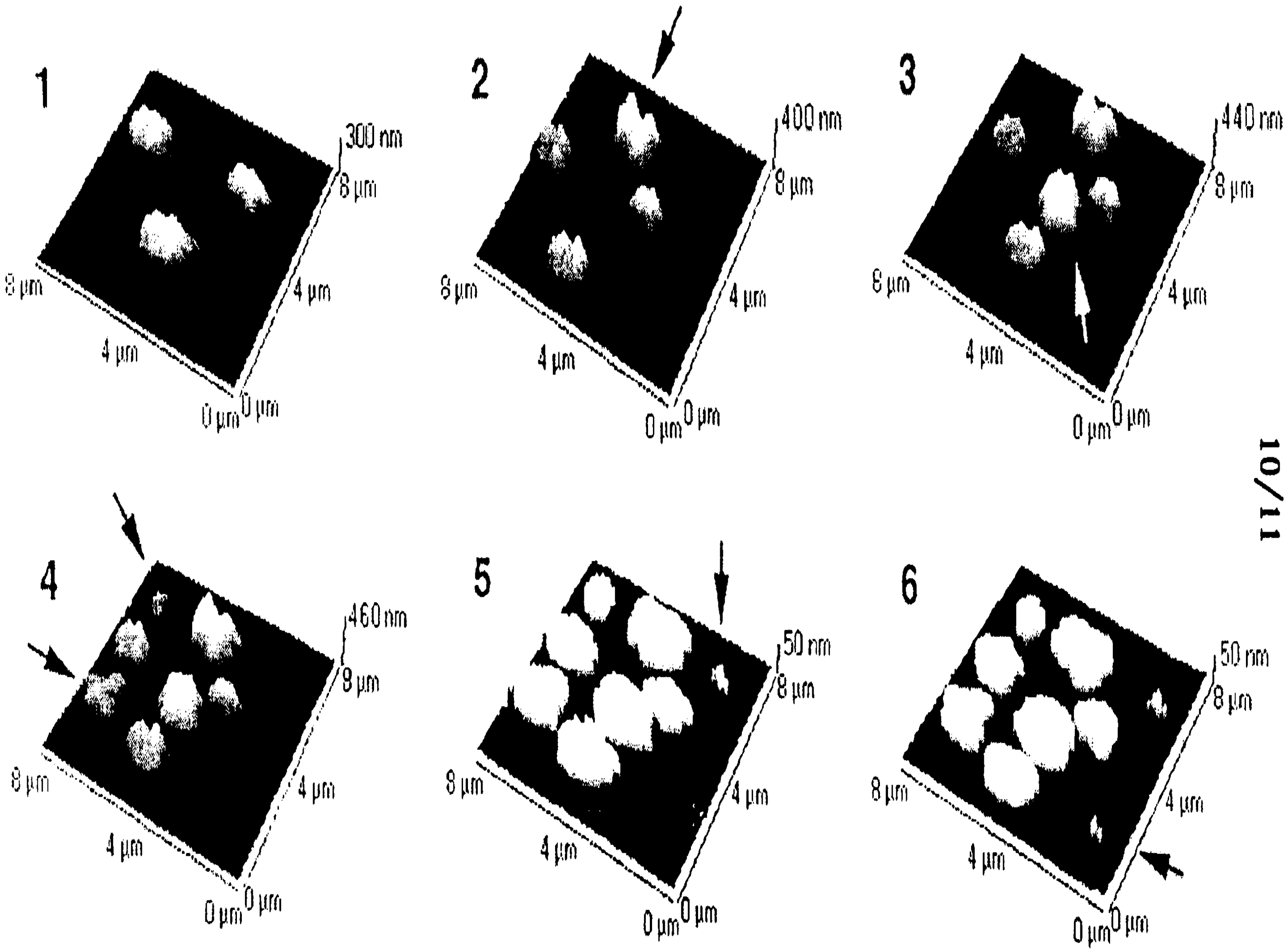
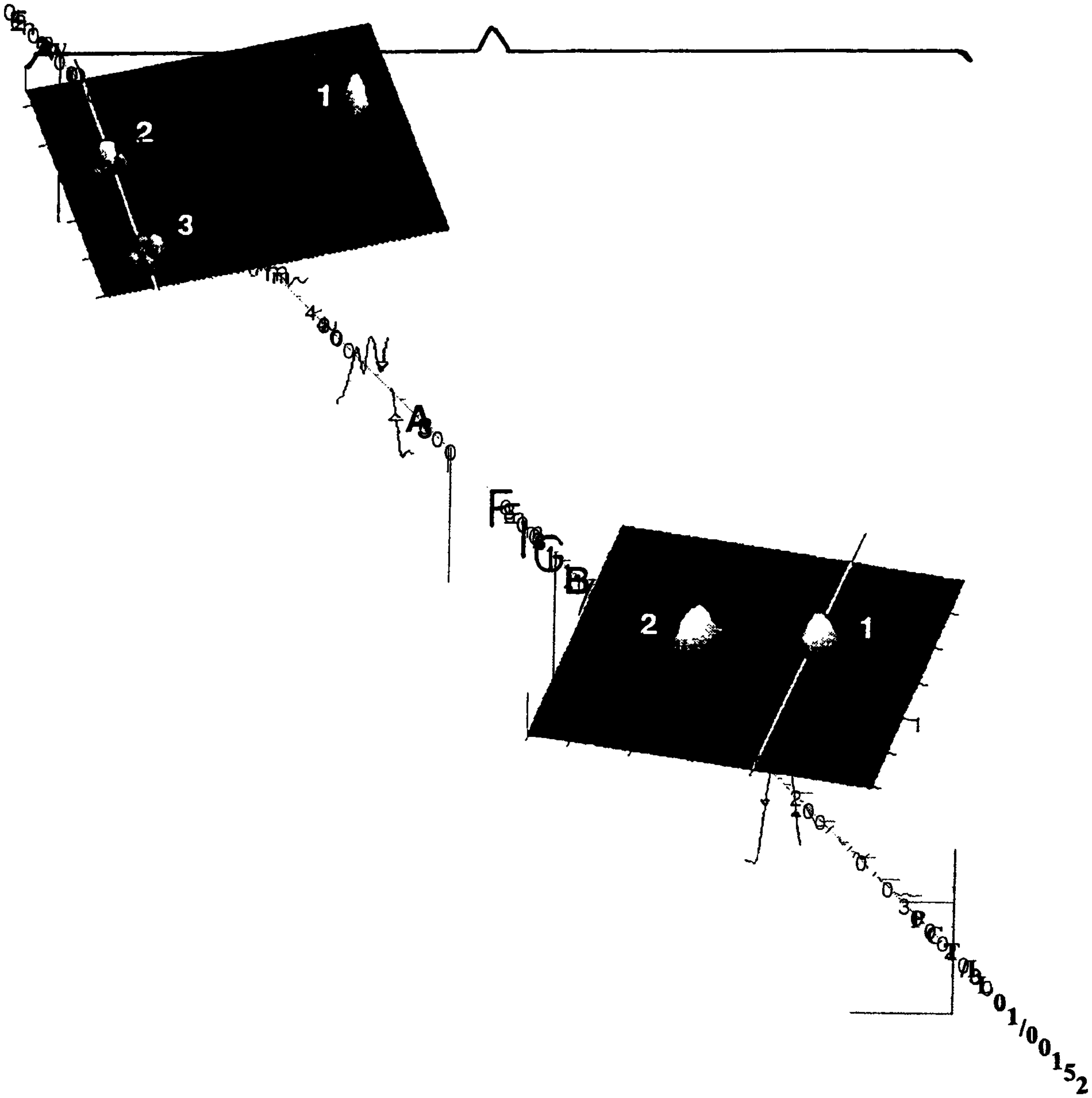

1
300 nm
8 µm
4 µm
0 µm
8 µm
4 µm
0 µm
2
400 nm
8 µm
4 µm
0 µm
8 µm
4 µm
0 µm
3
440 nm
8 µm
4 µm
0 µm
8 µm
4 µm
0 µm
4
460 nm
8 µm
4 µm
0 µm
8 µm
4 µm
0 µm
5
50 nm
8 µm
4 µm
0 µm
8 µm
4 µm
0 µm
6
50 nm
8 µm
4 µm
0 µm
8 µm
4 µm
0 µm

FIG. 9


A
1
2
3
B
2
1